CHAPTER 3

EPA/NSF ETV EQUIPMENT VERIFICATION TESTING PLAN FOR GRANULAR ACTIVATED CARBON ADSORPTION OF DISINFECTION BY-PRODUCT PRECURSORS

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1.0 APPLICATION OF THIS EQUIPMENT VERIFICATION TESTING PLAN

This document is an ETV Testing Plan for granular activated carbon (GAC) adsorption to be used within the structure provided by the document: "EPA/NSF ETV Protocol For Equipment Verification Testing Of Disinfection By-Product Precursor Removal: Requirements For All Studies". This Testing Plan is to be used as a guide in the development of a Product-Specific Test Plan for testing of GAC adsorption equipment to achieve removal of precursors of disinfection byproducts (DBPs). Refer to the ETV Protocol referenced above for further information.

In order to participate in the equipment verification process for GAC adsorption, the equipment Manufacturer and their designated Field Testing Organization (FTO) shall employ the procedures and methods described in this test plan and in the referenced ETV Protocol Document as guidelines for the development of a Product-Specific Test Plan (PSTP). The PSTP should generally follow those Tasks outlined herein, with changes and modifications made for adaptations to specific GAC adsorption equipment. At a minimum, the format of the procedures written for each Task should consist of the following sections:

- Introduction
- Experimental Objectives
- Work Plan
- Analytical Schedule
- Evaluation Criteria

The primary treatment goal of the equipment employed in this Verification Testing Program is to achieve removal of DBP precursors present in water supplies such that finished waters are of acceptable water quality. The experimental design of the PSTP shall therefore be developed so the relevant questions about water treatment equipment capabilities can be answered. Each PSTP shall include all of the included tasks, Tasks 1 to 5.

2.0 INTRODUCTION

Adsorption by GAC can be an effective treatment technique for removing DBP precursors prior to disinfection application. GAC contactors are operated as filters usually containing a 12x40 or 8x30 US Standard Mesh size GAC. They can be operated after rapid sand filtration (post-filter adsorber) or as a filter-adsorber, in which the GAC contactor also acts as a filter of particulate matter, and therefore must be backwashed after increases in headloss. Typical empty-bed contact times (EBCTs) are 10 to 30 minutes for post-filter adsorbers, and 5 to 10 minutes for filter-adsorbers.

GAC adsorption is an unsteady-state process. DBP precursor removal, as measured by total organic carbon (TOC) or ultraviolet absorbance at 254 nm (UV₂₅₄), is typically greater than 85 percent at the beginning of contactor operation for EBCTs greater than 10 minutes. Over time, effluent concentrations increase, yielding a characteristic breakthrough curve that is unique to the water source, pretreatment conditions, EBCT, and type of GAC used. Breakthrough curves can

also be developed for DBP precursors by chlorinating GAC effluent samples. Thus, the GAC contactor run time to a given effluent criterion can be determined from the appropriate breakthrough curve. Once effluent criteria are exceeded, the GAC must be replaced with new or reactivated GAC.

This Verification Testing Plan is not designed to evaluate the removal of preformed DBPs by GAC in treatment systems employing prechlorination. This Verification Testing Plan is designed to evaluate GAC performance for the removal of the precursors to DBPs formed by chlorination after GAC adsorption.

Continuous chlorine addition prior to GAC adsorption should be avoided when possible. GAC removes chlorine, and therefore chlorine must be reapplied after GAC to maintain a disinfectant residual in the distribution system. Chlorine added prior to GAC adsorption increases the level of DBPs in the finished water, while decreasing the ability of GAC to adsorb DBP precursors.

The test protocol has been designed to assess the GAC adsorption capacity. When utilizing the rapid small-scale column test (RSSCT), long-term biological removal of DBP precursors by GAC may not be well simulated, due to relatively short run times. However, unless preozonation is practiced, biological activity in a GAC column can effectively remove only 10 to 20 percent of the TOC or dissolved organic carbon (DOC) in groundwaters or treated surface waters. The remainder of the TOC removed is often attributed to bioactivity (another 5 to 10 percent), but is actually due to slow adsorption. The RSSCT has been calibrated and verified with the data from at least 30 full- or pilot-scale GAC columns (Summers et al., 1995). Since biological activity is inherent in all full- and pilot-scale GAC columns, its removal contribution does not seem to impact the breakthrough curve enough to warrant special consideration; the RSSCT well-simulates the breakthrough curve of non-preozonated waters. If, due to treatment processes in place prior to GAC (such as ozonation) or past experience with the water to be tested, it is felt that biological activity will play a significant role in determining GAC efficiency, then it is recommended that the package plant be utilized during testing.

This Verification Testing Plan is not intended to be used for the evaluation of ability of GAC to serve as a particulate matter (turbidity) filter. The ETV Testing Plan for Coagulation and Filtration should be used in conjunction with this Testing Plan when verification of particulate matter filtration performance is required.

3.0 GENERAL APPROACH

This Verification Testing Plan is centered on completion of two main tasks: System Integrity Verification Testing and Adsorption Capacity Verification Testing. System Integrity Verification Testing is a two-week field operation of the equipment with monitoring to ensure the system is functional and to identify any major systemic problems such as channeling, insufficient media, excessive headloss buildup, etc. This Testing Plan includes sampling and monitoring requirements for System Integrity Verification Testing. Adsorption Capacity Verification Testing is intended to evaluate the ability of the type of GAC and contact time utilized to remove DBP precursors to the level stated by the FTO. Such a statement by the FTO

might be phrased as: "This system, when operated at a GAC EBCT of 15 minutes or more, is capable of achieving an effluent TOC concentration below 2.0 mg/L for at least 50 days for GAC influent TOC concentrations between 3.0 and 4.0 mg/L and influent pH less than 8.0."

Testing shall be conducted by an NSF-qualified Field Testing Organization that is selected by the Manufacturer. Water quality analytical work to be completed as part of this ETV Testing Plan shall be contracted with an NSF-approved laboratory.

The influent water quality chosen for Adsorption Capacity Verification Testing should reflect the objectives the Manufacturer establishes on the equipment performance. Multiple performance objectives established regarding the ability of a system to treat a variety of influent water quality conditions must be supported by Adsorption Capacity Verification Testing performed under conditions representative of this range of water quality. Adsorption Capacity Verification Testing must be conducted at least once using the equipment. Subsequent testing may be performed in the field using the equipment or in a laboratory using the rapid small-scale column test (RSSCT), a rapid bench-scale GAC test. The RSSCT shall be designed to simulate the EBCT of the equipment and shall use a representative sample of the GAC used in the system.

The manufacturer shall stipulate which pretreatment processes are necessary prior to GAC adsorption. The recommended pretreatment processes shall then be employed as pretreatment during Equipment Verification Testing. GAC adsorption performance will be evaluated based on GAC influent water quality, sampled after any pretreatment processes. If Adsorption Capacity Verification Testing is conducted using RSSCTs, any Manufacturer recommended pretreatment processes must be simulated prior to the RSSCT. Alternatively, the water used as influent to the RSSCT may be sampled from a package plant or full-scale treatment plant employing representative recommended pretreatment process.

4.0 OVERVIEW OF TASKS

The following section provides a brief overview of the tasks included in the GAC Verification Testing Plan.

4.1 Task 1: System Integrity Verification Testing

The objectives of this task are to demonstrate that the equipment is (1) able to initially produce a finished water of acceptable quality, and (2) able to reliably operate under field conditions. The equipment is operated, monitored, and sampled for approximately two weeks.

4.2 Task 2: Adsorption Capacity Verification Testing

The objectives of this task are to evaluate the ability of the GAC equipment to meet the water quality objectives specified by the Manufacturer. The performance of the GAC system is a function of the type of GAC used and the influent water quality. Adsorption Capacity Verification Testing must be repeated, as necessary, using different water sources to verify the ability of the equipment to meet multiple treated water quality objectives stated by the Manufacturer. GAC influent and effluent DBP precursor surrogate analyses performed include TOC and UV₂₅₄. DBP precursor removal will also be assessed, by chlorination of GAC influent and effluent water samples. The duration of testing will depend on treatment goals supplied by the Manufacturer. Adsorption Capacity Verification Testing shall be performed at least once using the equipment. Thereafter, the RSSCT may be utilized for Adsorption Capacity Verification Testing.

4.3 Task 3: Documentation of Operating Conditions and Treatment Equipment Performance

During each day of Verification testing, operating conditions shall be documented. This shall include descriptions of any pretreatment processes and their operating conditions. In addition, the performance of the water treatment equipment shall be documented, including rate of filter head loss gain and frequency and duration of filter washing for GAC contactors operated as filter-adsorbers. The volumetric flow rate through a GAC contactor is a critical parameter, and shall be frequently monitored, recorded, and adjusted if necessary. GAC performance is affected by the EBCT, which is a function of the volumetric flow rate through the contactor.

4.4 Task 4: Data Management

This task will establish effective field protocol for data management at the field operations site and for data transmission between the Field Testing Organization and the NSF.

4.5 Task 5: Quality Assurance/Quality Control (QA/QC)

The objective of this task is to ensure accurate measurement of operational and water quality parameters during Verification testing.

5.0 TESTING PERIODS

Task 1, System Integrity Verification Testing, is designed to be carried out in conjunction with Tasks 3 through 5 in a two-week period, not including mobilization and start-up. Task 2, Adsorption Capacity Verification Testing, is designed to be carried out in conjunction with Tasks 3 through 5. The duration of Task 2 is dependent on the run time required to verify Manufacturer's treatment objectives, the source water quality, and whether testing is conducted using the system or the RSSCT. The expected duration of Adsorption Capacity Verification Testing may range from 1 to 6 months. Adsorption Capacity Verification Testing performed using the rapid bench-scale GAC test (RSSCT) decreases the testing period to between 5 and 15

percent of equipment testing, not including experimental design and set-up, obtaining a water source, and bench-scale pretreatment, if necessary.

6.0 **DEFINITIONS**

- **6.1 Bed volume:** a normalized unit of throughput, run time divided by EBCT.
- **6.2 Breakthrough curve:** a characteristic profile of a GAC adsorber. The effluent concentration of a parameter is plotted over time, typically showing a small amount of immediate breakthrough, a point of initial breakthrough where the effluent concentration begins to steadily increase over the immediate breakthrough, and a diminishing rate of increase over time.
- **6.3 BV**₅₀: throughput in number of bed volumes treated to 50 percent TOC breakthrough
- **6.4 Empty-bed contact time (EBCT):** retention time in an empty contactor
- **6.5 Immediate breakthrough:** a fraction of natural organic matter that is nonadsorbable, and can be quantified in the GAC effluent immediately after startup, usually at very low levels (0.1 0.5 mg/L TOC, typ.)
- **6.6 Initial breakthrough:** the point in GAC run time when effluent concentrations begin to increase above the nonadsorbable fraction concentration.
- **Rapid small-scale column test (RSSCT):** a scaled version of a GAC adsorber, utilizing a smaller particle size GAC, designed with scaling equations which maintain similitude to the full-scale system.
- **Run time:** the operation time of a GAC contactor to a given effluent criterion. For a system, the run time is given in days. For a RSSCT, actual laboratory run time is converted to "full-scale equivalent run time," due to the scaled design of the RSSCT.
- **6.9** t_{50} : run time to 50 percent TOC breakthrough

7.0 TASK 1: SYSTEM INTEGRITY VERIFICATION TESTING

7.1 Introduction

This task will evaluate the short-term ability of the equipment to produce water of acceptable quality. This task is not designed to evaluate the long-term ability of the system to remove DBP precursors.

7.2 Experimental Objectives

The objectives of this task are to demonstrate that the system is (1) able to initially produce a finished water of acceptable quality, and (2) able to reliably operate under field conditions.

7.3 Work Plan

The Manufacturer and their designated FTO shall specify the operating conditions to be evaluated during verification testing and shall supply written procedures on the operation and maintenance of the treatment system. To complete the System Integrity Test, the treatment system shall be operated continuously for a minimum of 344 hours (14 full days plus one 8-hour work shift). For GAC contactors operated in a filter-adsorber mode, the treatment equipment shall be operated from start-up until turbidity breakthrough or terminal head loss is attained, at which time the contactors shall be backwashed and operation shall resume. For GAC contactors operated as post-filter adsorbers, the media filters in-line upstream of the GAC contactors shall be operated from start-up until turbidity breakthrough or terminal head loss is attained, at which time the media filters shall be backwashed and operation shall resume. In either case, System Integrity Verification Testing shall include at least one backwashing event, as determined by turbidity breakthrough or terminal headloss. Verification testing using a water source that requires filter backwashing every 1 to 4 days is recommended. Interruptions in the treatment system shall be documented and are allowed only for backwashing events and required equipment maintenance. Since GAC performance is a function of EBCT, which is dependent on the volumetric flow rate, it is critical that verification testing be conducted at a set flow rate that is maintained within 5 percent of the design value.

GAC contactors operated as filter-adsorbers must meet ETV Testing for Filtration to be verified as a filter of particulate matter.

Water Quality Sample Collection. Water quality data shall be collected at regular intervals as described below in the Analytical Schedule. Additional or more frequent analyses may be stipulated at the discretion of the FTO. Sample collection frequency and protocol shall be defined by the FTO in the PSTP.

In the case of water quality samples to be shipped to the state-certified or third party- or EPA-accredited, off-site laboratory for analysis, the samples shall be collected in appropriate containers (containing preservatives as applicable) prepared by the off-site laboratory. These samples shall be preserved, stored, shipped, and analyzed in accordance with appropriate procedures and holding times, as specified by the analytical laboratory. Acceptable methods for the required analytical procedures are described in Task 5, Quality Assurance/Quality Control.

7.4 Analytical Schedule

7.4.1 Operational Data Collection

The FTO shall provide written procedures describing the operational parameters that should be monitored, monitoring points, and the frequency of monitoring. Such operational parameters shall include at a minimum system flow rates and head loss or pressure. The FTO shall include acceptable values and ranges for all operational parameters monitored.

7.4.2 Water Quality Data Collection

During System Integrity Testing, the GAC influent (feed) water quality and GAC effluent water quality shall be characterized by analysis of the water quality parameters listed in Table 1.

The first sampling for each required analyte shall be performed one day after plant operation start-up, and then by the frequency given. Although many parameters may be analyzed off-site, pH, temperature, and turbidity must be analyzed on-site. It is recommended that UV_{254} be also analyzed on-site.

The above water quality parameters are listed to provide readers of the verification report with background data on the quality of the feed water being treated and the quality of the treated water. These data are to be collected to enhance the acceptability of the System Integrity Verification Testing for a wide range of drinking water applications.

7.5 Evaluation Criteria and Minimum Reporting Requirements

The results of System Integrity Verification Testing shall be evaluated based on TOC and UV_{254} removal. For filter-adsorbers, turbidity removal shall also be evaluated. The Coagulation and Filtration Verification Testing Protocol shall be followed if the filter-adsorber is to be verified as a filter of particulate matter. Time series plots shall be generated describing GAC influent and effluent TOC, GAC influent and effluent UV_{254} , and GAC influent and effluent turbidity.

The removal by GAC of TOC and UV_{254} is indicative of the removal of DBP precursors: formed DBP breakthrough generally parallels TOC and UV_{254} breakthrough for a given water. The System Integrity Verification Testing should yield high percent removals of these analytes (low immediate breakthrough), demonstrating the initial ability of GAC to very effectively remove DBP precursor material. High levels of immediate breakthrough of TOC and UV_{254} are indicative of failure of the treatment system to initially remove DBP precursors, possibly due to hydraulic channeling, insufficient media, very low GAC adsorption capacity, or inappropriate GAC contactor design for the water quality tested. Long term DBP precursor control will be evaluated during Task 2 (Adsorption Capacity Verification Testing).

8.0 TASK 2: ADSORPTION CAPACITY VERIFICATION TESTING

8.1 Introduction

The purpose of System Integrity Verification Testing is to quickly and efficiently test the basic ability of the GAC contactor system (1) to initially yield a treated water of acceptable water quality and (2) to reliably operate under field conditions. Once this has been demonstrated, the long term effectiveness of the treatment system to remove DBP precursors shall be evaluated by Adsorption Capacity Verification Testing.

GAC treatment is an unsteady-state process whose ability to remove DBP precursors will diminish over time. The breakthrough of DBP precursors for a given water source is characteristic of the treatment system and will depend on design, EBCT, the type of GAC used, and influent water quality. Breakthrough is highly dependent on the concentration and adsorbability of DBP precursors to be treated by GAC. The Manufacturer may establish multiple objectives regarding the DBP precursor removal ability of the equipment, since GAC performance is dependent on influent water quality. To verify these objectives, the FTO shall repeat Adsorption Capacity Verification Testing, utilizing multiple water qualities representative of those described in the objectives, as described below in the Work Plan.

Adsorption Capacity Verification Testing shall be performed at least once for a system, but may be performed multiple times on different water qualities to verify the Manufacturer's objectives made on the ability of the equipment to remove DBP precursors under various influent water quality conditions.

After initial Adsorption Capacity Verification Testing is performed using the equipment, subsequent Adsorption Capacity Verification Testing may be performed either using the equipment or the rapid small-scale column test (RSSCT). The RSSCT is a scaled version of a GAC adsorber, utilizing a smaller particle size GAC, designed with scaling equations that maintain similitude to the full-scale system. A proportional diffusivity approach is used as diffusion to adsorption sites has been shown to be proportional to the GAC particle size. Therefore, run times to GAC effluent criteria are shortened by a factor proportional to the ratio of the full-scale GAC particle size to the RSSCT GAC particle size. The main advantage of the RSSCT approach is that run times are shortened to 5-20 percent of full-scale run times. A relatively small amount of water is needed, which can be transported to an off-site laboratory. Furthermore, the RSSCT approach does not require an evaluation of adsorption capacity and kinetics by separate experiments or the use of numerical or analytical models (Summers et al., 1995).

One drawback of the RSSCT stems from the use of a batch influent water sample: a single RSSCT experiment will not show the effects of long-term seasonal variability that may be captured during a full-scale run. The selection of a representative batch water sample for the RSSCT is extremely important as changes in influent concentration and adsorbability can lead to misleading results as compared to full-scale GAC adsorber results. Removal of DBP precursors in a full-scale GAC contactor by biodegradation may not be simulated by an RSSCT, due to relatively short run times required by the RSSCT.

After initial Adsorption Capacity Verification Testing is performed using the equipment, Adsorption Capacity Verification Testing may be performed either by use of the equipment, or by RSSCTs designed to simulate the treatment conditions utilized in the equipment. Manufacturers interested in verifying multiple objectives based on treatment of varying GAC influent water qualities may find that Adsorption Capacity Verification Testing performed using a series of RSSCTs will decrease the time and effort required to assess system performance for DBP precursor removal.

8.2 Experimental Objectives

The objectives of this task are to evaluate the ability of the GAC contactors and treatment system to meet the water quality objectives specified by the Manufacturer.

The Manufacturer and FTO shall identify the treated water quality objectives to be achieved in the statement of performance objectives of the equipment to be evaluated during verification testing. The manufacturer's performance objective(s) is used to establish data quality objectives (DQOs) in order to develop the experimental design of the verification test. The broader the performance objective(s), the more comprehensive the PSTP must become to achieve the DQOs. The Manufacturer shall also identify in the statement of performance objectives the specific DBPs that shall be monitored during verification testing. The statement of performance objectives prepared by the Manufacturer shall indicate the range of water quality under which the equipment can be challenged while successfully treating the GAC influent water. Two examples of satisfactory statements for demonstration of water treatment capabilities are provided below:

- 1. "This system, when operated at a GAC EBCT of 15 minutes or more, is capable of maintaining an treated water TOC concentration below 1.0 mg/L for up to 60 days in GAC influent waters with TOC concentrations between 2.0 and 3.0 mg/L and with GAC influent water pH below 8.0."
- 2. "This system, when operated at a GAC EBCT of 15 minutes or more, is capable of maintaining treated water formed total trihalomethanes and the sum of six haloacetic acids under uniform formation conditions below 40 and 30 μg/L, respectively, for up to 60 days in GAC influent waters with TOC concentrations between 2.0 and 3.0 mg/L and with GAC influent water pH below 8.0."

8.3 Work Plan

The FTO shall specify run time criteria for each Adsorption Capacity Verification Testing period. Run time criteria can be based on treated water quality conditions, or set to a specific maximum run time. For example, the FTO may specify that the equipment be operated until the effluent TOC concentration reaches 2.0 mg/L. Alternatively, the FTO may specify a maximum run time of 60 days. A combination of treated water quality and maximum run time criteria may also be utilized.

The run time criteria chosen should reflect the treatment objectives of the system, based on the GAC influent water quality. Therefore, water sources must be chosen carefully so that water qualities are representative of that upon which the Manufacturer's treatment objectives are based. Specifically, the measured influent formed DBP concentration or DBP precursor surrogate

concentration (e.g., TOC) during verification esting must average within 20 percent of the amount stated in the Manufacturer's treatment objectives. This stipulation ensures that Adsorption Capacity Verification Testing adequately tests the equipment's ability to meet Manufacturer's objectives for a given water quality. Multiple Adsorption Capacity Verification Testing periods will be necessary to provide verification testing on multiple treatment capability objectives. For example, a minimum of five Adsorption Capacity Verification Testing runs are required to inclusively verify water treatment objectives made on water qualities with GAC influent TOC concentrations ranging between 1.0 and 7.0 mg/L. GAC performance is also affected by the pH of the GAC influent water. Therefore, Adsorption Capacity Verification Testing shall be performed at a GAC influent pH as close as possible to the pH stated in the water treatment objectives. A tolerance of \pm 0.2 pH units is acceptable.

8.3.1 Equipment Operation

In assessing equipment, Adsorption Capacity Verification Testing may begin simultaneously with System Integrity Verification Testing. Subsequent sessions of Adsorption Capacity Verification Testing will not require System Integrity Verification Testing. The FTO shall specify the operating conditions to be utilized during verification testing and shall supply written procedures on the operation and maintenance of the treatment system.

8.3.2 RSSCT Operation

The RSSCT shall be designed using scaling equations derived based on proportional diffusivity assumptions. The design equations for RSSCTs are included in the *Granular Activated Carbon Precursor Removal Studies* section of the *ICR Manual for Bench- and Pilot-Scale Treatment Studies* (USEPA, 1996). The GAC used for the RSSCT shall be a representative sample of unused virgin or reactivated GAC used in the equipment. The RSSCT shall be designed to simulate the EBCT utilized in the equipment.

Various sources for the influent water to be used for the RSSCT studies are possible. If pretreatment modules (e.g. coagulation and sand filtration) are included prior to GAC as a part of the equipment, then this water may be sampled during steady-state operation of these treatment steps has been reached and used as influent to the RSSCT. An existing full-scale water treatment system may also be sampled if treatment steps and DBP precursor removal is representative of that achieved by the equipment. This would allow for the sampling of different water sources and qualities without necessitating transportation, set-up, and operation of the equipment to generate the RSSCT influent water. Alternatively, raw water may be sampled and batch treated under conditions that simulate treatment and DBP precursor removal by the equipment prior to GAC adsorption. In all cases, bench-scale filtration of the RSSCT influent water through a prerinsed 1.0-µm glass fiber cartridge filter is required.

It is preferable that the batch influent collected for the RSSCT be large enough to provide a water source of constant water quality for the duration of each RSSCT run. The influent water sampling frequency for the RSSCT is based on a minimum number of samples taken per water batch spaced evenly over the RSSCT run. If more than one water batch is sampled for a RSSCT study, than influent sampling requirements will increase.

Depending on design and run time, an RSSCT typically requires 100 to 300 L of influent water. The *Granular Activated Carbon Precursor Removal Studies* section of the *ICR Manual for Bench- and Pilot-Scale Treatment Studies* (Treatment Studies Manual) contains guidance in Sections 5.1, 5.2, and 5.3 regarding RSSCT design, operation, and monitoring. The procedures contained in the Treatment Studies Manual shall be followed when performing RSSCTs, with the following exceptions:

- Design of the RSSCT shall be based on the actual EBCT utilized for GAC adsorption in the equipment. The Treatment Studies Manual specifies that RSSCTs be designed with full-scale equivalent EBCTs of 10 and 20 minutes. For verification testing, RSSCTs must be designed based on the system GAC contactor EBCT under normal operating conditions.
- 2. The RSSCT influent water should ideally be sampled from the equipment after all treatment steps that remove DBP precursors but prior to GAC adsorption. If water samples are taken from an existing water treatment plant, then all treatment steps performed on and chemicals added to the water sample must be representative of the equipment, including prechlorination. If raw water is sampled and batch treated in an off-site laboratory, then the batch treatment must simulate the treatment conditions, chemical dosages, and resulting DBP precursor removal of the pretreatment steps in the equipment.
- 3. The Treatment Studies Manual does not allow chlorine addition as part of the RSSCT influent water pretreatment (prechlorination). It is not necessary to avoid prechlorination for the purposes of Adsorption Capacity Verification Testing. However, the presence of prechlorination will require sample analysis of formed DBPs in the RSSCT influent and effluent before further chlorination testing.
- 4. Sampling and analytical methods must be performed as described below in the Analytical Schedule section of Adsorption Capacity Verification Testing.
- 5. The FTO shall specify a run time criteria for each Adsorption Capacity Verification Testing period. Run time criteria can be based on treated water quality conditions, or set to a specific maximum run time. A run time to 70 percent TOC breakthrough, as specified in the Treatment Studies Manual, is not required.
- 6. Performing quarterly RSSCT sessions to capture seasonal variability for a given water source (as required in the Treatment Studies Manual) is not necessary. However, multiple RSSCT runs on different water sources with varying water qualities may be necessary to verify the Manufacturer's objectives made on the ability of the equipment to remove DBP precursors under a range of water quality conditions.

8.4 Analytical Schedule

8.4.1 Operational Data Collection

The FTO shall provide written procedures describing the operational parameters that should be monitored, monitoring points, and the frequency of monitoring. Such operational parameters shall include at a minimum system flow rates and head loss or pressure. The FTO shall include acceptable values and ranges for all operational parameters monitored.

8.4.2 Water Quality Data Collection

During Adsorption Capacity Verification Testing utilizing either the equipment or the RSSCT, the GAC influent (feed) water quality and GAC effluent water quality shall be characterized by analysis of the water quality parameters listed in Table 2.

The sampling frequency described in Table 2 is intended to provide sufficient operational data and to effectively characterize the breakthrough profile of DBP precursors. A minimum of eight evenly-spaced GAC effluent samples must be analyzed for TOC, UV₂₅₄, and DBP formation after chlorination under uniform formation conditions (UFC). (See Task 5 for a description of and procedures for UFC chlorination). The DBPs analyzed after UFC chlorination shall be those upon which the manufacturer's objectives of equipment performance are based. Additionally, optional analysis of DBPs not included as part of the manufacturer's objectives may be analyzed. These DBPs include, but are not limited to, those listed as optional in Table 2. For pretreatment processes that include prechlorination, additional blank or instantaneous DBP samples must be analyzed. By doing so, the breakthrough of DBPs present in the influent to GAC water (preformed DBPs) can be distinguished from the formation of DBPs after further chlorination testing.

In addition to the required UFC chlorination to assess DBP formation as described above, selected site-specific simulated distribution system (SDS) conditions may be used. SDS conditions may be used to evaluate DBP precursor removal by GAC under varying site-specific distribution system conditions, such as a higher temperature or longer residence times. Chlorination under SDS conditions does not replace the required chlorination under UFC conditions.

The exact sampling interval will depend on the length of verification testing. If the verification testing run time is specified by the FTO as a length of time (e.g., 60 days or 60 full-scale equivalent days) then the required number of samples shall be taken in evenly spaced intervals throughout the verification testing period. If verification testing run time is specified by the FTO as an effluent water quality criterion only, then a run time estimate is needed to determine the appropriate sampling interval.

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¹All references to run times in the following discussion are full-scale run times. The discussion is applicable to both full-scale (package plant) and RSSCT studies, but run times need to be scaled down for application to RSSCT studies.

A flow diagram detailing a procedure to generate a run time estimate is shown in Figure 1. This procedure is based on correlating a given GAC effluent TOC concentration to the influent TOC concentration and run time. If an effluent TOC criterion is not given, then the run time estimate is determined by estimating the TOC concentration from the given formed DBP effluent criterion. Specific DBP yields for 10 different water sources are tabulated in Summers et al. (1996), and average specific DBP yields are listed in Table 3. An estimate of the TOC concentration can be obtained by dividing the DBP concentration by the average specific DBP yield.

A correlation has been shown between GAC run time and influent TOC concentration for 28 case studies from 21 different source waters. These studies include bench-, pilot-, and full-scale breakthrough profiles using bituminous-based GAC for waters with influent TOC concentrations between 1 and 11 mg/L and initial pH values between 7 and 8. Surface and ground waters from across the U.S. are included in the data set comprising the correlation. A best fit of the data is described by Equation 1 (Summers et al., 1994; Hooper et al., 1996):

$$BV_{50} = \frac{18,000}{TOC_0} \qquad r^2 = 0.86 \tag{1}$$

where BV_{50} is the number of bed volumes treated to 50 percent TOC breakthrough and TOC_0 is the influent TOC concentration (mg/L). The run time to 50 percent TOC breakthrough, t_{50} , is calculated by multiplying BV_{50} and the EBCT:

$$BV_{50} \times EBCT = t_{50} \tag{2}$$

Using Equations 1 and 2, t_{50} can now be calculated:

$$t_{50} = \frac{BV_{50} * EBCT (min)}{1440 (min/day)}$$
 (3)

where t₅₀ is the run time to 50 percent TOC breakthrough (days) and 1440 is a conversion factor between units of minutes and days. Substituting into Equation 1:

$$t_{50} = \frac{12.5 * EBCT}{TOC_0}$$
 (4)

Equation 4 is only applicable for a run time estimate if the run time criteria is an effluent TOC concentration near 50 percent of the influent TOC concentration. When the run time criteria yields an effluent TOC concentration other than 50 percent of the influent TOC concentration, Equation 4 can still be used, by introduction of a constant:

$$t_{P} = \frac{12.5 * A_{P} * EBCT}{TOC_{0}}$$
 (5)

where \mathfrak{b} is run time to percent breakthrough P, and A_P is a constant whose value is determined from Table 4 or Figure 2, and is based on the percent TOC breakthrough goal. For example, given a GAC run time criteria of an effluent TOC concentration of 2.4 mg/L, corresponding to 60 percent TOC breakthrough in a system with a TOC₀ of 4.0 mg/L, a value for A_P of 1.28 should be used in Equation 5. For an EBCT of 15 min, this would yield an estimated run time of 60 days (full-scale or full-scale equivalent).

Once a run time estimate has been determined, sampling events for TOC, UV_{254} , and DBP formation assessment shall be evenly spaced throughout the run time, after an initial sampling one day after the start of operation. The sampling interval can be calculated by Equation 6:

$$I_{S} = \frac{t_{P} - 1}{n_{S} - 1} \tag{6}$$

where I_S is the sampling interval (days) and n_S is the number of samples. For RSSCTs, the sampling interval must be scaled down by the appropriate factor to yield a laboratory sampling interval. In addition, initial sampling should begin after no less than one hour of RSSCT operation.

The above procedure has been developed to provide an estimate of GAC run time based on influent water quality and FTO's run time criterion, assuming a water quality with average DBP precursor adsorbability, average specific DBP yield, the use of a bituminous based GAC, and an influent pH between 7 and 8. Run times may exceed the estimate for highly adsorbable water sources or influent pH values below 6.5. If no maximum run time is stipulated by the FTO, then verification testing should proceed until the effluent water quality criterion is met or exceeded, regardless of the calculated estimated run time. It may be prudent to include a 20 percent safety factor in the run time estimate calculation when the relative adsorbability of the water source is unknown.

Additional parameters or more frequent analysis of the some of the above parameters may be required to ensure that pretreatment steps included prior to GAC are functioning properly. Additional sampling requirements, acceptable analytical methods, and sampling frequencies shall be provided by the FTO.

The first sampling event for each required analyte shall be performed one day after operation start-up, (one hour for RSSCTs) and then by the frequency given. Although many parameters may be analyzed off-site, pH, temperature, and turbidity must be analyzed on-site. It is recommended that UV_{254} be also analyzed on-site. Samples to be assessed for DBP formation should be chlorinated as soon as possible after the sampling event. In general, samples should be chlorinated no later than 5 days after each sample was taken. The water quality parameters in Table 2 are listed to provide verification report readers with background data on the quality of the feed water being treated and the

quality of the treated water. These data are to be collected to enhance the acceptability of the Adsorption Capacity Verification Testing for a wide range of drinking water applications.

8.5 Evaluation Criteria and Minimum Reporting Requirements

8.5.1 Control of TOC, UV₂₅₄, and DBP Formation

Plot breakthrough curves (GAC effluent concentrations versus run time) for TOC, UV_{254} , and UFC-DBP concentrations. Include plotted GAC influent parameter concentrations over run time on the same plot. Calculate and tabulate average influent parameter concentrations. Compare DBP precursor removal with Manufacturer-specified removal goals.

8.5.2 Process Control

Tabulate or plot GAC influent and effluent temperature, pH, and turbidity. Include GAC influent and effluent average, standard deviation, and percent standard deviation for each analyte. Tabulate GAC influent alkalinity, calcium hardness, and total hardness. Include average, standard deviation, and percent standard deviation for each analyte.

9.0 TASK 3: DOCUMENTATION OF OPERATING CONDITIONS AND TREATMENT EQUIPMENT PERFORMANCE

9.1 Introduction

During each day of verification testing, operating conditions shall be documented. This shall include descriptions of any pretreatment processes and their operating conditions. In addition, the performance of the water treatment equipment shall be documented, including rate of filter head loss gain and frequency and duration of filter washing for GAC contactors operated as a filter-adsorber. The volumetric flow rate through a GAC contactor is a critical parameter, and must be monitored and documented. GAC performance is affected by the EBCT, which varies directly with the volumetric flow rate through the contactor.

9.2 Experimental Objectives

The objective of this task is to accurately and fully document the operation conditions that applied during treatment, and the performance of the equipment. This task is intended to result in data that describe the operation of the equipment and data that can be used to develop cost estimates for operation of the equipment.

This task shall be performed in conjunction with System Integrity Verification Testing. This task shall also be performed in conjunction with Adsorption Capacity Verification Testing, when Adsorption Capacity Verification Testing is conducted using the equipment. When Adsorption Capacity Verification Testing is conducted using RSSCTs, a summary description of the

pretreatment applied to the water sampled for each RSSCT session shall be provided, including pretreatment steps, chemical dosages, flow rates, and any other relevant design and process information. In addition, a design summary of the RSSCT shall also be provided, including, but not limited to, particle size, scaling factor, column diameter, bed depth, volumetric flow rate, EBCT, velocity, minimum Reynolds number, porosity, dry bed density, and mass of GAC utilized.

9.3 Work Plan

During each day of verification testing (both System Integrity Verification Testing and Adsorption Capacity Verification Testing), treatment equipment operating parameters for both pretreatment and GAC adsorption shall be monitored and recorded on a routine basis. This shall include a complete description of pretreatment chemistry; mixing and flocculation intensities, if applicable; operating parameters for clarification ahead of filtration, if applicable; rate of flow; and filtration rate. Data on filter head loss and backwashing shall be collected for either sand media prefilter or GAC filter-adsorber.

Electrical energy consumed by the treatment equipment shall be measured, or as an alternative, the aggregate horsepower of all motors supplied with the equipment could be used to develop an estimate of the maximum power consumption during operation. Performance shall be evaluated to develop data on chemical dosages needed and on energy needed for operation of the process train being tested.

A complete description of each treatment process shall be given, with data on points of chemical addition, and volume and detention time of each process basin at rated flow, if applicable. Data on the GAC contactor shall be provided and shall include the EBCT, depth, effective size, and uniformity coefficient of each layer of GAC and support material. The type and source of GAC used and the type of support material used shall be stated.

9.4 Schedule

Table 5 presents the schedule for observing and recording equipment operating and performance data. The schedule applies to both System Integrity Verification Testing and Adsorption Capacity Verification Testing using the equipment. For Adsorption Capacity Verification Testing conducted using the RSSCT, Table 6 presents the schedule for observing and recording RSSCT operating and performance data.

9.5 Evaluation Criteria

Where applicable, the data developed from this task shall be compared to Manufacturer's statements of performance objectives. If no relevant statement of performance objectives exists, results of operating conditions and performance data will be tabulated for inclusion in the Verification Report.

10.0 TASK 4: DATA MANAGEMENT

10.1 Introduction

The data management system used in the verification testing program shall involve the use of computer spreadsheet software and manual recording of operational parameters for the GAC adsorption and pretreatment equipment on a daily basis.

10.2 Experimental Objectives

The Objective of this task is to establish a viable structure for the recording and transmission of field testing data such that the Field Testing Organization provides sufficient and reliable operational data for verification purposes.

10.3 Work Plan

The following protocol has been developed for data handling and data verification by the Field Testing Organization. Where possible, a Supervisory Control and Data Acquisition (SCADA) system should be used for automatic entry of testing data into computer databases. Specific parcels of the computer databases for operational and water quality parameters should then be downloaded by manual importation into Excel (or similar spreadsheet software) as a comma delimited file. These specific database parcels shall be identified based upon discrete time spans and monitoring parameters. In spreadsheet form, the data shall be manipulated into a convenient framework to allow analysis of GAC contactor operation. At a minimum, backup of the computer databases to diskette should be performed on a monthly basis.

In the case when a SCADA system is not available, field testing operators shall record data and calculations by hand in laboratory notebooks. (Daily measurements shall be recorded on specially-prepared data log sheets as appropriate.) The laboratory notebook shall provide carbon copies of each page. The original notebooks shall be stored on-site; the carbon copy sheets shall be forwarded to the project engineer of the Field Testing Organization at least once per week during each quarterly one-month testing period. This protocol will not only ease referencing the original data, but offer protection of the original record of results. Operating logs shall include a description of the treatment equipment (description of test runs, names of visitors, description of any problems or issues, etc.); such descriptions shall be provided in addition to experimental calculations and other items.

The database for the project shall be set up in the form of custom-designed spreadsheets. The spreadsheets shall be capable of storing and manipulating each monitored water quality and operational parameter from each task, each sampling location, and each sampling time. All data from the laboratory notebooks and data log sheets shall be entered into the appropriate spreadsheet. Data entry shall be conducted on-site by the designated field testing operators. All recorded calculations shall also be checked at this time. Following data entry, the spreadsheet shall be printed out and the print-out shall be checked against the handwritten data sheet. Any corrections shall be noted on the hard-copies and corrected on the screen, and then a corrected

version of the spreadsheet shall be printed out. Each step of the verification process shall be initialed by the field testing operator or engineer performing the entry or verification step.

Each experiment (i.e., System Integrity Verification Testing runs or Adsorption Capacity Verification Testing runs) shall be assigned a unique run number which will then be permanently associated to the data from that experiment through each step of data entry and analysis. As samples are collected and sent to state-certified or third party- or EPA- accredited laboratories, the data shall be tracked by use of the same system of run numbers. Data from the outside laboratories shall be received and reviewed by the field testing operator. These data shall be entered into the data spreadsheets, corrected, and verified in the same manner as the field data.

11.0 TASK 5: QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

11.1 Introduction

Quality assurance and quality control of the operation of the water treatment system, GAC contactors, RSSCTs, and the measured water quality parameters shall be maintained during the verification testing program.

11.2 Experimental Objectives

The objective of this task is to maintain strict QA/QC methods and procedures. When specific items of equipment or instruments are used, the objective is to maintain the operation of the equipment or instructions within the ranges specified by the Manufacturer or by *Standard Methods*. Maintenance of strict QA/QC procedures is important, in that if a question arises when analyzing or interpreting data collected for a given experiment, it will be possible to verify exact conditions at the time of testing.

11.3 Work Plan

Equipment flow rates and associated signals should be documented and recorded on a routine basis. A routine daily walk through during testing shall be established to verify that each piece of equipment or instrumentation is operating properly. Particular care shall be taken to confirm that any chemicals are being fed at the defined flow rate into a flowstream that is operating at the expected flow rate, such that the chemical concentrations are correct. In-line monitoring equipment such as flowmeters, etc. shall be checked to verify that the readout matches with the actual measurement (i.e. flow rate) and that the signal being recorded is correct. The items listed are in addition to any specified checks outlined in the analytical methods or specified by the FTO.

It is extremely important that system flow rates be maintained at set values and monitored frequently. Doing so allows a constant and known EBCT to be maintained in the GAC contactor or RSSCT. GAC performance is directly affected by the EBCT, which in turn is proportional to the volumetric flow rate through the contactor or RSSCT. Therefore, an important QA/QC objective shall be the maintenance of a constant volumetric flow rate through the GAC contactor

or RSSCT by frequent monitoring and documentation. Documentation shall include an average and standard deviation of recorded flow rates through the GAC contactor or RSSCT.

11.3.1 Daily QA/QC Verifications:

- Chemical feed pump flow rates (verified volumetrically over a specific period of time)
- In-line turbidimeter flow rates (verified volumetrically over a specific period of time, if employed)
- In-line turbidimeter readings checked against a properly calibrated bench model.
- System GAC contactor flow rate (verified volumetrically every two hours when staffed; at least twice daily)
- RSSCT column flow rate (verified volumetrically every two hours when staffed; at least three times daily)

11.3.2 QA/QC Verifications for Each Testing Period:

- In-line flow meters/rotameters (clean equipment to remove any debris or biological buildup and verify flow rate volumetrically to avoid erroneous readings)
- In-line turbidimeters (clean out reservoirs and recalibrate)
- Differential pressure transmitters (verify gauge readings and electrical signal using a pressure meter)
- Tubing (verify good condition of all tubing and connections, replace if necessary)

11.4 On-Site Analytical Methods

The analytical methods utilized in this study for on-site monitoring of GAC influent and effluent water quality are described in the section below. Use of either bench-top or in-line field analytical equipment will be acceptable for the verification testing; however, in-line equipment is recommended for ease of operation. Use of in-line equipment is also preferable because it reduces the introduction of error and the variability of analytical results generated by inconsistent sampling techniques.

11.4.1 pH

Analyses for pH shall be performed according to Standard Method 4500-H⁺ or EPA Method 150.1/150.2. A three-point calibration of the pH meter used in this study shall be performed once per day when the instrument is in use. Certified pH buffers in the expected range shall be used. The pH probe shall be stored in the appropriate solution defined in the instrument manual. Transport of carbon dioxide across the air-water interface can confound pH measurement in poorly buffered waters. If this is a problem, measurement of pH in a confined vessel is recommended to minimize the effects of carbon dioxide loss with the atmosphere.

11.4.2 Temperature

Temperature shall be analyzed according to *Standard Method* 2550. The thermometer shall have a scale marked for every 0.1 °C, as a minimum, and should be calibrated weekly against a precision thermometer certified by the National Institute of Standards and Technology (NIST). (A thermometer having a range of -1°C to +51°C, subdivided in 0.1° increments, would be appropriate for this work.)

11.4.3 UV₂₅₄ Absorbance

Analysis of UV_{254} shall be performed according to *Standard Method* 5910 B. The maximum allowable holding time for *Standard Method* 5910 B is 48 hours. Therefore, it is recommended that UV_{254} samples be analyzed on-site by the Field Testing Organization with an UV spectrophotometer at 254 nm.

11.4.4 Turbidity

Turbidity analyses shall be performed according to *Standard Method* 2130 or EPA Method 180.1 with either a bench-top or in-line turbidimeter. In-line turbidimeters are recommended for measurement of turbidity in the treated water, and either an in-line or a bench-top turbidimeter may be used for measurement of the feedwater.

During each verification testing period, the bench-top and in-line turbidimeters will be left on continuously. Once each turbidity measurement is complete, the unit will be switched back to its lowest setting. All glassware used for turbidity measurements will be cleaned and handled using lint-free tissues to prevent scratching. Sample vials will be stored inverted to prevent deposits from forming on the bottom surface of the cell.

The Field Testing Organization shall be required to document any problems experienced with the monitoring turbidity instruments, and shall also be required to document any subsequent modifications or enhancements made to monitoring instruments.

Bench-top Turbidimeters: Grab samples shall be analyzed using a bench-top turbidimeter. Readings from this instrument will serve as reference measurements throughout the study. The bench-top turbidimeter shall be calibrated within the expected range of sample measurements at the beginning of equipment operation and on a weekly basis using primary turbidity standards of 0.1, 0.5, and 3.0 Nephlometric Turbidity Units (NTU). Secondary turbidity standards shall be obtained and checked against the primary standards. Secondary standards shall be used on a daily basis to verify calibration of the turbidimeter and to recalibrate when more than one turbidity range is used.

The method for collecting grab samples will consist of running a slow, steady stream from the sample tap, triple-rinsing a dedicated sample beaker in this stream, allowing the sample to flow down the side of the beaker to minimize bubble entrainment, double-rinsing the sample vial with the sample, carefully pouring from the beaker down

the side of the sample vial, wiping the sample vial clean, inserting the sample vial into the turbidimeter, and recording the measured turbidity.

For the case of cold water samples dial cause the vial to fog preventing accurate readings, allow the vial to warm up by submersing partially into a warm water bath for approximately 30 seconds.

In-line Turbidimeters: In-line turbidimeters must be calibrated and maintained as specified in the manufacturer's operation and maintenance manual. It will be necessary to verify the in-line readings using a bench-top turbidimeter at least daily; although the mechanism of analysis is not identical between the two instruments the readings should be comparable. Should these readings suggest inaccurate readings then all in-line turbidimeters should be recalibrated. In addition to calibration, periodic cleaning of the lens should be conducted, using lint-free paper, to prevent any particle or microbiological build-up that could produce inaccurate readings. Periodic verification of the sample flow should also be performed using a volumetric measurement. Instrument bulbs should be replaced on an as-needed basis. It should also be verified that the LED readout matches the data recorded on the data acquisition system, if the latter is employed.

11.5 Chemical and Biological Samples Shipped Off-Site for Analyses

The analytical methods that shall be used during testing for chemical and biological samples that are shipped off-site for analyses are described in the section below.

11.5.1 Inorganic Samples

Inorganic chemical samples shall be collected and preserved in accordance with *Standard Method* 3010B, if applicable, paying particular attention to the sources of contamination as outlined in *Standard Method* 3010C. The samples shall be refrigerated at approximately 4°C immediately upon collection, shipped in a cooler, and maintained at a temperature of approximately 4°C during shipment. Samples shall be held and processed for analysis by a State or EPA-accredited laboratory in accordance with *Standard Methods*. The laboratory shall keep the samples at approximately 4°C until initiation of analysis.

Alkalinity analyses shall be performed according to Standard Method 2320 B. Calcium hardness analyses shall be performed according to Standard Method 3500-Ca D. Total hardness analyses shall be performed according to Standard Method 2340 C. In accordance with Standard Method 2340 B, total hardness may also be analyzed by addition of separate analyses of calcium and magnesium. Calcium and magnesium may be analyzed by Standard Method 3111B, Standard Method 3120 or EPA Method 200.7.

11.5.2 Organic Parameters: Total Organic Carbon (TOC)

TOC analyses shall be performed according to Standard Method 5310 C. Samples for analysis of TOC shall be collected in amber glass bottles with TFE-lined septa supplied by the State or EPA accredited laboratory. The appropriate preservative as indicated by the State or EPA accredited laboratory shall be added. The samples shall be shipped overnight with an internal cooler temperature of approximately 4°C to the analytical laboratory. Samples shall be processed for analysis by the State or EPA accredited laboratory within 24 hours of collection. The laboratory shall then keep the samples at a temperature of 4°C until initiation of analysis.

11.5.3 DBP Samples

DBPs samples shall be collected, preserved (if applicable), held, and analyzed in accordance with the appropriate Standard Method.

11.6 Tests and Data Specific to GAC Type Evaluated

The GAC type used for testing shall be described by providing data on the GAC type characteristics and tests listed in Table 7. All analyses shall be performed according to procedures outlined in AWWA B-604.

11.7 DBP Precursor Assessment Test Protocol

During Adsorption Capacity Verification Testing, GAC adsorption of DBP precursors shall be assessed by simulating full-scale disinfection and sampling for DBPs. This is accomplished by spiking water samples with disinfectant and holding the spiked samples headspace-free in the dark at a designated temperature, pH, and contact time. Both GAC influent and effluent samples are tested, thus allowing for DBP precursor removal through GAC contactors to be assessed.

In practice, drinking water utilities and researchers often test for DBP formation under site-specific simulated distribution system (SDS) conditions. Under SDS conditions, the disinfectant dose, disinfectant residual, contact time, temperature, and pH utilized are representative a particular distribution system. For Adsorption Capacity Verification Testing, DBP formation shall be assessed under uniform formation conditions (UFC) with free chlorine as disinfectant. The UFC test is a free chlorine residual-based test that uses constant chlorination conditions representative of average distribution system conditions (Summers et al., 1996). The constant chlorination conditions used will facilitate DBP precursor control comparisons between Adsorption Capacity Verification Testing sessions performed on different water sources and different systems. The UFC test conditions are:

• Incubation time: 24 ± 1 hours • Incubation temperature: 20.0 ± 1.0 °C • Buffered pH: 8.0 ± 0.2

• 24-hr free chlorine residual: 1.0 ± 0.4 mg/L as Cb

An important aspect of the UFC test is that it is based on a constant free chlorine residual after the 24-hour incubation time. However, free chlorine demand (chlorine dose subtracted from free chlorine residual) varies with water sources and with treatment, based on differences in inorganic and organic demand. In general, as TOC increases, free chlorine demand increases.

Some difficulty may be encountered when attempting to achieve the target UFC free chlorine residual for GAC effluent samples, as the unsteady-state behavior of GAC is reflected in free chlorine demand. This difficulty is heightened by the presence of inorganic compounds, which may exert a significant free chlorine demand, and are not removed by GAC. If inorganic demand is significant, then it may account for a large fraction of the overall free chlorine demand present at the beginning of the breakthrough curve, when organic free chlorine demand is well removed by the GAC. As run time increases, organic demand increases while inorganic free chlorine demand remains constant, thus diminishing the effect of inorganic demand on overall free chlorine demand.

For GAC effluent samples, free chlorine demand usually correlates well with TOC concentration, and this relationship can be utilized to aid in predicting free chlorine demand, without directly accounting for inorganic demand. If prior experience with GAC adsorption relating free chlorine demand to TOC for a particular water source and pretreatment is not available, a method has been developed that simulates breakthrough conditions to obtain a relationship between free chlorine demand and TOC throughout GAC contactor run time. The method is published in the Treatment Studies Manual (USEPA, 1996a) and an adaptation has been included in Appendix A.

Alternatively, a sample to be chlorinated may be split into three incubation bottles and chlorinated under UFC. The chlorine dose is varied across the three samples, with the goal of obtaining at least one sample with the targeted 24-hour free chlorine residual of 1.0 ± 0.4 mg/L as Cb. After 24 hours, the free chlorine residual is measured in all three samples, and the sample with an acceptable free chlorine residual is also sampled for the FTO-specified DBP analyses. When the approximate chlorine dose is known, it is also acceptable to chlorinate a small aliquot of the sample under UFC, and to measure only the free chlorine residual of the aliquot after 24 hours. Based on the measured free chlorine demand, adjustments are made, if necessary, to the required chlorine dose for UFC, and the rest sample is chlorinated.

During UFC chlorination, the following parameters shall be recorded: chlorine dose (mg/L as Cl₂); free chlorine residual (mg/L as Cl₂); initial sample pH, just prior to chlorine addition; final sample pH, at end of incubation period; incubation temperature (°C); incubation time (hours).

The chlorine stock solution shall be standardized according to Standard Method 4500-Cl B. The stock solution is typically prepared at a concentration 500 to 1000 times stronger than the dose required to minimize dilution errors. Free chlorine residual shall be analyzed according to Standard Method 4500-Cl D, 4500-Cl F, 4500-Cl G, or 4500-Cl H. Prior to and after chlorination, pH shall be analyzed according to Standard Method 4500-H⁺ B or EPA Method 150.1/150.2. Temperature shall be analyzed according to Standard Method 2550 B.

DBP analysis shall be performed by a state or EPA accredited laboratory according to Standard Methods and EPA procedures appropriate for the designated DBPs. The bottles used to sample for DBPs shall be prepared by the state or EPA accredited laboratory, and shall contain all required quenching agents and preservatives.

A standard operating procedure for UFC chlorination has been published (Summers et al., 1996) and is contained in Appendix B.

12.0 OPERATION AND MAINTENANCE

The Field Testing Organization shall obtain the Manufacturer-supplied operations and maintenance (O&M) manual to evaluate the instructions and procedures for their applicability during the verification testing period. The following are recommendations for criteria for the evaluation of O&M manuals for equipment employing granular activated carbon for DBP precursor removal

12.1 Maintenance

The manufacturer should provide readily understood information on the required or recommended maintenance schedule for each piece of operating equipment including, but not limited to:

- pumps
- valves
- all instruments, such as turbidimeters or pH meters
- water meters, if provided
- pressure or headloss gauges

The manufacturer should provide readily understood information on the required or recommended maintenance schedule for non-mechanical or non-electrical equipment including, but not limited to:

- GAC contactor vessels
- feed lines
- manual valves

The manufacturer should provide readily understood information on the following procedures:

• spent GAC removal and replacement

12.2 Operation

The manufacturer should provide readily understood information on the required or recommended procedures related to the proper operation of the equipment, including, but not limited to, the following aspects:

GAC filtration:

• control of filtration rate

• observation and measurement of head loss during filter run (only applicable to GAC filter-adsorbers)

Backwashing (only applicable to GAC filter-adsorbers):

- determination of end of filter-adsorber run
- use of auxiliary water scour (surface wash) or air scour
- start of backwash
- appropriate backwash rates and times
- conclusion of backwashing
- return of contactor to service

Monitoring and observing operation:

- measuring feed water flow rates
- feed water turbidity
- filtered water turbidity
- contactor head loss
- procedures to follow upon turbidity breakthrough (only applicable to GAC filter-adsorbers)

13.0 REFERENCES

Hooper, S.M., R.S. Summers, G. Solarik, and S. Hong. 1996. GAC Performance for DBP Control: Effect of Influent Concentration, Seasonal Variation, and Pretreatment. In *Proc. of the AWWA Annual Conference*, Toronto, Ontario, Canada.

Standard Methods for the Examination of Water and Wastewater. 1999. 20th edition. APHA, AWWA, and WEF, Washington, D.C.

Summers, R.S., S.M. Hooper, H.M. Shukairy, G. Solarik, and D.M. Owen. 1996. Assessing DBP Yield: Uniform Formation Conditions. *Journal AWWA* (88:6:80).

Summers, R.S., S.M. Hooper, G. Solarik, D.M. Owen, and S. Hong. 1995. Bench-Scale Evaluation of GAC for NOM Control. *Journal. AWWA* (87:8:69).

Summers, R.S., S. Hong, S.M. Hooper, and G. Solarik. 1994. Adsorption of Natural Organic Matter and Disinfection By-Product Precursors. In *Proc. of the AWWA Annual Conference*, New York, NY.

USEPA. 1996a. ICR Manual for Bench- and Pilot-Scale Treatment Studies. Technical Support Division, Office of Ground Water and Drinking Water, U.S. Environmental Protection Agency.

USEPA. 1996b. DBP/ICR Analytical Methods Manual. Technical Support Division, Office of Ground Water and Drinking Water, U.S. Environmental Protection Agency.

Table 1.

Required water quality analyses and minimum sample frequencies for System Integrity Verification Testing

Parameter	Frequency	Standard Method ^a	EPA Method ^b	
GAC Influent				
Temperature	Weekly	2550 B		
pН	Once daily	4500-H ⁺ B	150.1 / 150.2	
Alkalinity	Weekly	2320 B		
Total hardness	Weekly	2340 C		
Calcium hardness	Weekly	3500-Ca D		
Total organic	Three samples evenly spaced over	5310 C		
carbon	testing period			
UV absorbance at	Three samples evenly spaced over	5910 B		
254 nm	testing period			
Turbidity	Filter-adsorber: continuous, and daily	2130 B / Method 2	180.1	
	at bench-top to check continuous			
	turbidimeter			
	Post-filter adsorber: daily			
GAC Effluent				
Temperature	Weekly	2550 B		
pН	Once daily	4500-H ⁺ B	150.1 / 150.2	
Total organic	Three samples evenly spaced over	5310 C		
carbon	testing period			
UV absorbance at	Three samples evenly spaced over	5910 B		
254 nm	testing period			
Turbidity	Filter-adsorber: continuous, and daily	2130 B / Method 2	180.1	
	at bench to check continuous			
	turbidimeters			
	Post-filter adsorber: daily			

<u>Notes</u>

^a Standard Methods Source: 20th Edition of <u>Standard Methods for the Examination of Water and Wastewater</u>, 1999, American Water Works Association.

^b EPA Methods Source: EPA Office of Ground Water and Drinking Water. EPA Methods are available from the National Technical Information Service (NTIS).

Table 2.

Required water quality analyses and minimum sample frequencies for Adsorption Capacity Verification Testing

Parameter	Frequency	Standard Method ^a	EPA Method ^b
GAC Influent			
Temperature	System: Weekly RSSCT: 3 evenly-spaced samples per water batch	2550 B	
рН	System: Twice weekly RSSCT: 3 evenly-spaced samples per water batch	4500-H ⁺ B	150.1 / 150.2
Alkalinity	System: 5 evenly-spaced sample events RSSCT: 3 evenly-spaced samples per water batch	2320 B	
Total hardness	System: 5 evenly-spaced sample events RSSCT: 3 evenly-spaced samples per water batch	2340 C	
Calcium hardness	System: 5 evenly-spaced sample events RSSCT: 3 evenly-spaced samples per water batch	3500-Ca D	
Total organic carbon	System: 8 sampling events ^c RSSCT: 3 sampling events ^d	5310 C	
UV absorbance at 254 nm	System: 8 sampling events ^c RSSCT: 3 sampling events ^d	5910 B	
Turbidity	System, filter adsorber: continuous, and daily at bench to check continuous turbidimeters System, post-filter adsorber: daily RSSCT: 3 evenly-spaced samples per water batch	2130 B / Method 2	180.1
Ammonia (optional)	System: 5 evenly-spaced sample events RSSCT: 3 evenly-spaced samples per water batch		
UFC-DBPs	System: 8 sampling events ^c RSSCT: 3 sampling events ^d		
Optional DBPs (if not already analyzed) ^e including THMs, HAA, TOX, chloral hydrate, chloropicrin, and haloacetonitriles	System: 8 sampling events ^c RSSCT: 3 sampling events ^d		
Preformed or instantaneous DBPs (if applicable) ^f	System: 8 sampling events ^c RSSCT: 3 sampling events ^d		
Bromide	System: 8 sampling events described RSSCT: 3 sampling events described		300.0

Table 2.

Required water quality analyses and minimum sample frequencies for Adsorption Capacity Verification Testing (continued)

		8 ()	
GAC Effluent			
Temperature	Weekly	2550 B	
pН	Twice weekly	4500-H ⁺ B	150.1 / 150.2
Total organic carbon	8 sampling events	5310 C	
UV absorbance at	8 sampling events	5910 B	
254 nm			
Turbidity	System filter adsorber: continuous, and	2130 B / Method 2	180.1
	daily at bench to check continuous		
	turbidimeters		
	System post-filter adsorber: daily		
	RSSCT: Not required		
Ammonia (optional)	System: 5 evenly-spaced sample events		
	RSSCT: 3 evenly-spaced samples per		
	water batch		
UFC-DBPs	8 sampling events		
Optional DBPs (if not	8 sampling events		
already analyzed) ^e			
including THMs,			
HAA, TOX, chloral			
hydrate, chloropicrin,			
and haloacetonitriles			
Preformed or	8 sampling events		
instantaneous DBPs	- -		
(if applicable) ^f			

Notes:

^a Standard Methods Source: 20th Edition of <u>Standard Methods for the Examination of Water and Wastewater</u>, 1999, American Water Works Association.

^b EPA Methods Source: EPA Office of Ground Water and Drinking Water. EPA Methods are available from the National Technical Information Service (NTIS).

^cInfluent sampling shall occur at approximately the same time as effluent sampling for each parameter during equipment operation.

^dRSSCT influent sampling shall be evenly spaced for each batch of water used throughout the run time.

^eDBPs included as part of manufacturer's objectives are not optional and must be analyzed. If not already analyzed, other optional DBPs may be analyzed. These DBPs include, but are not limited to, those listed.

^fIf pretreatment includes prechlorination, then the concentrations of preformed DBPs must be determined by analyzing blank or instantaneous DBP samples as described in section 8-4.

Table 3.
Average DBP specific yield under UFC (Summers et al., 1996)

UFC-DBP	Average Specific Yield (µg
	DBP/mg TOC)
TTHM	29
HAA6	19
TOX	99

Table 4.
Values of A_P to be used in Equation 5 for percent TOC breakthrough criteria

percent 100 breaking ough criteria		
Effluent TOC concentration	A_{P}	
as a percent (P) of influent		
TOC concentration (%)		
20	0.56	
30	0.68	
40	0.80	
50	1.00	
60	1.28	
70	1.80	

Table 5. Schedule for observing and recording equipment operating and performance data

Operational parameter	Action
Feed water and GAC contactor	When staffed, check and record every two hours, adjust
volumetric flow rate	when >5% above or below target. Record before and after adjustment.
GAC contactor head loss	Filter-adsorber: record initial clean bed total head loss at start of filter-adsorber run and record total head loss every two hours, when staffed. Post-filter adsorber: record daily
Filter backwash (filter-adsorber only)	Record time and duration of each filter washing. Record volume used to wash filter.
Electric power	Record meter daily
Chemicals used	Record name of chemical, supplier, commercial strength, dilution used for stock solution to be fed (if diluted) for all chemicals fed during treatment
Chemical feed volume and dosage	Check and record every 2 hours. Refill as needed and note volumes and times of refill
RPM of rapid mix and flocculator (if applicable)	Check daily and record
Hours operated per day	Record in log book at end of day or at beginning of first shift on the following work day. Any stoppage of flow to the contactors shall be recorded. Flow stoppage that exceeds 2 hour per 24-hour period or 7 hours per week shall be accounted for by not including it in the cumulative operation time.

Table 6. Schedule for observing and recording RSSCT operating and performance data

Operational parameter	Action
RSSCT flow rate	When staffed, check and record every two hours, adjust when >5% above or below target. Record before and after adjustment.
System pressure	When staffed, record every two hours
Hours operated per day	Record in logbook at end of day or at beginning of first shift on the following work day. Any stoppage of flow to the RSSCT shall be recorded. Flow stoppage that exceeds 30 minutes per 24-hour period shall be accounted for by not including it in the cumulative operation time.

Table 7.
Tests and data specific to GAC type evaluated

Data	Parameter
Raw material used to make GAC:	
Method of manufacture:	Chemical activation
	Thermal activation
	Agglomerated and activated
	Direct activation
Reactivated carbon:	Chemical activation
	Thermal activation
	Agglomerated
	Direct activation
Physical and chemical characteristics:*	Iodine number
	Percent ash
	Water soluble ash
	Abrasion number
	Moisture (weight %)
	Particle size
	Sieve size, US sieve series
	Effective size
	Uniformity coefficient

^{*}Tests used to determine values for physical and chemical characteristics must be performed in accordance with procedures outlined in AWWA B-604.

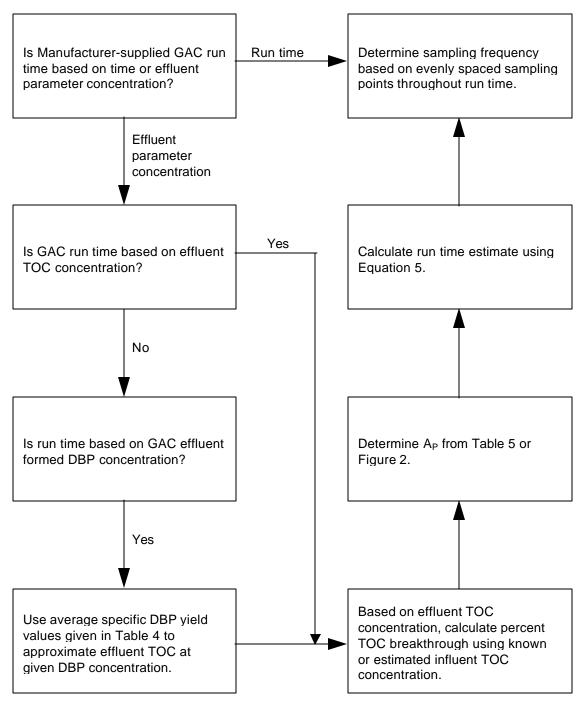
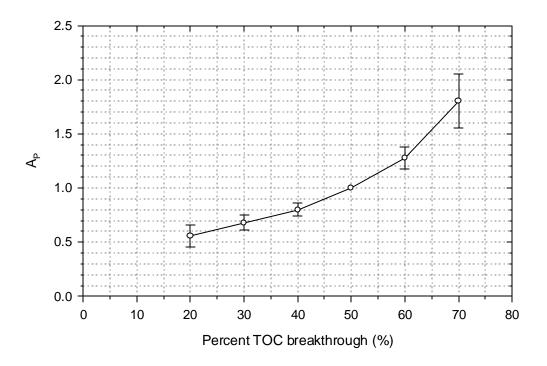


Figure 1.
Flow chart for determination of sampling frequency during Adsorption Capacity Verification Testing



 $\label{eq:Figure 2.} \textbf{ Values of A_P as a function of percent TOC breakthrough}$

Appendix A

Preliminary UFC Free chlorine Demand Study

If prior experience relating free chlorine demand to TOC for a GAC treated water from a specific source and with specific pretreatment is not available, a method has been developed that simulates breakthrough conditions to obtain a relationship between free chlorine demand and TOC, without requiring the operation of a separate GAC column. The method is termed a dilution study, and is based on diluting the GAC influent water to several intermediate TOC concentrations and investigating the free chlorine demand of these dilution samples. While TOC is diluted, the inorganic background should not be affected by the procedure. This is accomplished by diluting the GAC influent with water taken from the GAC effluent very early in GAC operation, so that natural organic matter removal is maximized and inorganic constituents are conserved.

The following outlines the dilution study procedure. Two aliquots of water are needed: one from the GAC influent, and one from the GAC effluent (dilution aliquot) taken as early as possible in the study, so that natural organic matter removal is maximized. The two aliquots are systematically mixed to form seven dilution samples with varying composition, as outlined in Table A-1. The volume of each dilution sample should be sufficient for TOC and UV_{254} analysis and to chlorinate at three doses for UFC free chlorine demand analysis. The total volume of the dilution aliquot is 50 percent greater than the required volume of GAC influent water. After mixing, each of the seven dilution samples are analyzed for TOC and UV_{254} . Three chlorine doses for each dilution sample are determined by multiplying the measured TOC of the dilution sample (TOC_{ds}) by the respective free chlorine demand (CD) to TOC ratio (CD:TOC) listed in Table A-1 and adding to these values the free chlorine residual required for the UFC test.

Chlorine dose = $TOC_{ds}(CD:TOC)$ + target free chlorine residual

Therefore, the chlorine dose for each dilution sample is bracketed with the goal of achieving a residual in one of the three samples that is near the target free chlorine residual. Note that at low TOC concentrations (dilution samples 1 through 3), a wide range of free chlorine demand to TOC ratios are used, because inorganic demand may dominate.

Dilution study chlorination should be conducted under UFC. The free chlorine demand calculated from the dose that yields a residual nearest to the target residual for each dilution sample is used to generate a plot of free chlorine demand against TOC. Thus, a correlation is obtained between TOC and free chlorine demand, which can be used to estimate free chlorine demand for GAC effluent samples, after TOC analysis.

Prior to chlorination for DBP analysis, it is recommended that a small aliquot from each effluent sample be chlorinated at a dose based on the dilution study results and analyzed only for free chlorine demand. Adjustments in the chlorine dose can then be made if needed, since the adsorbability or chlorine reactivity can naturally change with time.

Table A-1. Dilution study parameters

Sample number	Influent water	Dilution water	CD:TOC (mg Ch/mg TOC)		
	(%)	(%)	Low	Target	High
1	0	100	0.5	2.5	5.0
2	10	90	0.5	2.0	3.5
3	20	80	0.5	1.5	2.5
4	35	65	0.3	1.3	2.3
5	50	50	0.3	1.0	1.7
6	70	30	0.3	1.0	1.7
7	100	0	0.3	1.0	1.7

Appendix B

Uniform Formation Conditions (UFC) for DBP Formation Standard Operating Procedure (Summers et al., 1996)

Uniform Formation Conditions:

pH: 8.0 ± 0.2 temperature: 20.0 ± 1.0 °C incubation time: 24 ± 1 hr

free chlorine residual: 1.0 ± 0.4 mg/L as free chlorine after 24 hr

Preliminary Study:

A 24-hour free chlorine demand study on the water sample may be required before dosing under UFC to determine the applied dose that will yield a free chlorine residual of 1.0 mg/L after 24 hours (procedure described below).

Materials:

- chlorine demand-free glassware
- pH 8.0 borate buffer
- pH 8.0 combined hypochlorite/buffer dosing solution

Methods:

Chlorine demand-free glassware:

Incubation bottles (amber, with TFE-faced caps): soak in detergent (Fisher FL-70, 2%) at least overnight, rinse 4x with hot tap water, 2x with DI water. Place in 10-20 mg/L chlorine solution (made with DI water) for at least 24 hours. Rinse 4x with DI water and then 1-2x with type 1 reagent water (Standard Method 1080 C); dry in 140°C oven at least overnight. Store dosing pipettes in ~50 mg/L Cl₂ (made with type 1 reagent water). Rinse 3x with dosing solution prior to use, and return pipettes to storage in chlorine solution after use.

pH 8.0 borate buffer:

Before dosing, water samples are buffered to pH 8.0 with 2 mL/L borate buffer: 1.0M boric acid (ACS grade) and 0.26M sodium hydroxide (ACS grade) in boiled type 1 reagent water. If necessary, add diluted H_2SO_4 and NaOH by drops to the water samples after the buffer has been added for a final adjustment to pH 8.0. This buffer system is suggested; another buffer system, which does not exert a free chlorine demand and maintains sample pH at 8.0 ± 0.2 is acceptable.

pH 8.0 combined hypochlorite/buffer dosing solution:

A combined hypochlorite/buffer solution (based on method described in Koch et al., "A Simulated Distribution System Trihalomethane Formation Potential Method," 1987 AWWA WQTC) is made by buffering the hypochlorite solution to pH 8.0 with pH 6.7 borate buffer.

- pH 6.7 borate buffer: 1.0M boric acid (ACS grade) and 0.11M sodium hydroxide (ACS grade) in boiled type 1 reagent water
- add pH 6.7 borate buffer to chlorine solution (1000-4000 mg Cb/L) to yield a pH 8.0 dosing solution. (A 4-5:1 volume ratio of pH 11.2 hypochlorite solution to pH 6.7 borate buffer has been found to yield a pH 8.0 combined hypochlorite/buffer solution, with an approximately 20% drop in chlorine strength.)

The dosing solution (combined OCI/buffer) chlorine strength should allow for a dosing volume of < 0.5% of the water sample volume (e.g. 2.5 mL dosing solution in 1.0 L bottle).

Preliminary study:

Perform a 24-hour free chlorine demand study (buffered at pH 8.0 and incubated in the dark at 20°C as described in the dosing procedure) using a series of three chlorine doses based on C½:TOC ratios of 1.2:1, 1.8:1, and 2.5:1, after adjusting for inorganic demand. From the results of these tests, the chlorine dose for UFC is selected to yield a 24-hour residual of 1.0 mg/L free chlorine.

Dosing procedure:

- 1. add 2.0 mL/L pH 8.0 borate buffer to water sample
- 2. adjust to pH 8.0 with diluted H₂SO₄ and NaOH (if necessary)
- 3. fill incubation bottle 75 90 percent full with buffered water sample
- 4. dose with combined hypochlorite/buffer solution holding pipette just above water surface
- 5. cap bottle, invert twice
- 6. fill to top with buffered water sample and cap headspace-free
- 7. invert 10 times
- 8. incubate in dark at 20.0°C for 24 hours
- 9. after incubation period, measure free chlorine residual, pH, and sample for DBPs.

The following elements shall be considered for UFC chlorination:

- A. How close did experimental measurements of chlorination conditions (chlorine residual, incubation time, incubation pH, etc.) match the target conditions? Were they within the acceptable +/- range given for the UFC test?
- B. How much time elapsed between sampling and chlorination? A good guide is that samples should be chlorinated as soon as possible, but not more than 5 days after sample collection.
- C. After sampling, but prior to chlorination, samples should be stored in the dark at 4 degrees Celsius.

- D. When possible, DBPs should be sampled before chlorine residual and pH are measured.
- E. When sampling for more than one DBP, order of sampling should be based on relative volatility of compounds to be analyzed, with those most volatile sampled first. For example, THMs, TOX, and HAAs should be sampled in that order.